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(54) Solvent extraction of cuprous ions
from aqueous solutions

(57) Copper values are recovered from
aqueous solutions containing cuprous
ion, ferrous ion and halide or pseudo
halide ion, especially from solutions
derived from leaching of complex sul-
phide ores with ferric chloride or cupric
chloride, by (1) contacting the aqueous
solution with a solution in a water-
immiscible solvent of a suitable metal
extractant, (2) separating the aqueous
and organic phases and (3) contacting
the organic phase with an aqueous strip
solution containing cupric ion and
halide or pseudo-halide anion.

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SPECIFICATION

Process for the extraction of metal values

5 This invention relates to a process for the extraction of metal values from aqueous solutions of metal salts, and in particular to a process for the extraction of copper from aqueous solutions containing cuprous and ferrous cations and halide or pseudo-halide anions. 5

The use of solvent extraction techniques for the hydrometallurgical recovery of metal values from metal ores has been practised commercially for a number of years. For example copper may be recovered from 10 oxide ores or from ore tailings by treating the crushed ore with sulphuric acid to give an aqueous solution of copper sulphate which is subsequently contacted with a solution in a water-immiscible solvent of a metal extractant whereby the copper values are selectively extracted into the organic solvent phase. 10

The application of solvent extraction techniques to aqueous solutions containing halide ions has however hitherto presented numerous technical problems.

15 Of particular importance in this connection is the development of hydrometallurgical routes (as an alternative to smelting) for the extraction of copper from complex sulphide ores (including polymetallic sulphide ores) such as chalcopyrite. It is known to leach such ores using for example aqueous ferric chloride or cupric chloride solution, but the solvent extraction of the resultant leach solution presents formidable difficulties. Furthermore, whilst there may be process advantages in producing a leach solution containing 20 copper substantially in the form of cuprous ion, such leach solutions are especially difficult to treat by solvent extraction techniques. 20

According to the present invention there is provided a process for recovering copper values from an aqueous solution containing cuprous and ferrous cations and halide or pseudo halide anions which comprises the steps of

25 (1) contacting the aqueous solution with a solution in a water-immiscible organic solvent of a copper extractant capable of extracting cuprous ion in the presence of halide or pseudo halide ion; 25
 (2) separating from the aqueous phase the organic phase containing cuprous ion in the form of a halide- or pseudo halide-containing complex with the copper extractant; and
 (3) contacting the organic phase containing the complex of cuprous ion with the extractant with an 30 aqueous strip solution containing copper substantially in the form of the cupric ion and halide or pseudo-halide anion, whereby copper transfers from the organic phase into the aqueous strip solution, the relative concentrations of cupric ion and halide or pseudo-halide anion being such that the cuprous ion transferred into the aqueous strip solution is soluble therein. 30

The process of the present invention is especially suitable for the treatment of aqueous solutions derived 35 from the leaching of complex sulphide ores using ferric chloride or cupric chloride solutions as leachant. Whilst the leach conditions may be selected to provide a range of ratios of cuprous to cupric ion in the resultant leach solution, there are certain process advantages in providing a leach solution containing copper substantially as cuprous ion (for example copper in the form of cuprous ion containing less than 10% of cupric ion). Typical stoichiometry for such a leach processes is represented by the equations:

40 (a) $\text{CuFeS}_2 + 3\text{FeCl}_3 = \text{CuCl} + 4\text{FeCl}_2 + 2\text{S}$ 40
 (b) $\text{CuFeS}_2 + 3\text{CuCl}_2 = 4\text{CuCl} + \text{FeCl}_2 + 2\text{S}$

45 In the course of the extraction, elemental sulphur is precipitated and is separated from the aqueous leach solution. The resultant leach solution, which contains copper substantially in the form of cuprous ion, and iron substantially in the form of ferrous ion (for example iron in the form of ferrous ion containing less than 10% of ferric ion) may form the feed for the process of the present invention. In general, there will be sufficient ferrous chloride present in solution to prevent precipitation of cuprous chloride, but if necessary 50 additional halide ion may be added to solubilise the cuprous ion. Such halide ion may be added for example in the form of alkali metal or alkaline earth metal chloride. The ferric chloride leachant solution should be sufficiently acid to prevent precipitation of hydrated oxides of iron, and a typical leach solution derived from such a process may contain for example 50 gpl cuprous ion, 3M ferrous chloride and 0.2M hydrochloric acid. Typical leach conditions using cupric chloride as leachant and typical resultant leach solutions are described 55 for example in United States Patent 3,901,776.

In stage (1) of the process of the present invention, the aqueous solution containing cuprous ion, ferrous ion and halide or pseudo-halide ion, for example a solution derived from the leaching of a complex sulphide ore with ferric chloride solution, is contacted with a solution in a water-immiscible organic solvent of a copper extractant. Suitable copper extractants capable of extracting cuprous ion in the presence of halide or 60 pseudo-halide ion are substituted pyridines described in our European Patent No. 0 057 797. The substituted pyridine extractants described in the European Patent are capable of extracting either cupric or cuprous ions. However, we have found that cuprous ion generally forms a stronger complex with the extractant which is in consequence relatively more difficult to strip. We therefore prefer to use a relatively "weak" extractant, for example an alkyl diester of pyridine-3,5-dicarboxylic acid wherein the alkyl groups of the diester contain a 65 total of from 16 to 36 carbon atoms. 65

Suitable water-immiscible organic solvents are well known in the art, and may be for example aliphatic, aromatic and alicyclic hydrocarbons. The concentration of the extractant in the water-immiscible organic solvent may be chosen to suit the particular leach solution to be treated. Typical values of extractant concentration in the organic phase are between about 0.1 to 2 Molar, and an especially convenient range is 5 from 0.2 to 0.8 molar in the organic solvent.

The separation step (2) in the process of the present invention may be undertaken using conventional means, for example conventional settlers.

In step (3) in the process of the present invention, the organic solution containing the extractant complex is contacted with an aqueous strip solution containing cupric ion and halide or pseudohalide anion into which 10 the cuprous ion is transferred. The relative concentrations of the cupric and halide or pseudo-halide anion are such that the cuprous ion is transferred into the aqueous strip solution and is soluble therein. The 15 molarity of halide or pseudo-halide anion required may be readily determined from standard solubility curves for a given concentration of cuprous and cupric ion. Typically, a strip solution capable of removing about 15 gpl of cuprous ion from the organic phase will contain about 25 gpl cupric ion, and will be about 20 0.75 M in hydrochloric acid. In the course of the steps (1) to (3), cuprous ion is substantially separated from undesirable impurities originally present in the leach solution, and from the iron leachant. The resultant pregnant strip solution contains an increased concentration of purified cuprous ion from which metallic 25 copper may be recovered as described hereafter. Preferably the aqueous strip solution is the barren solution obtained after metallic copper is removed from the pregnant strip solution. In this way one driving force 30 causing the cuprous ion to transfer from the organic extractant phase to the aqueous strip solution is the depletion of copper in the strip solution. An additional driving force may be provided at certain chloride ion concentrations if, as will generally be the case, chloride ion is also removed from pregnant strip solution during the course of the recovery of metallic copper from the cuprous ion.

A variety of methods are available for the recovery of metallic copper from the pregnant strip solution. In a 25 first example of such a method, the pregnant strip solution is passed to the cathode compartment of a split electrolytic cell in which the cathode compartment is separated from the anode compartment by an anion exchange membrane. The operation of such a split cell is described in US Department of the Interior Bureau of Mines Report RI 8007. Into the anode compartment is passed ferrous chloride solution, which is preferably the aqueous leach solution from which cuprous ion has been removed in the extraction step (1) of the 30 process of the present invention. In this way, the cuprous ion is electrodeposited in the cathode compartment as pure cathode copper, whilst the associated halide or pseudo-halide ion transfers through the anion exchange membrane to the anode compartment where the ferrous ion is oxidised to ferric ion. The 35 spent electrolyte from the cathode compartment, which now contains substantially only cupric ion and a reduced concentration of halide or pseudo-halide ion associated with the removal of cuprous ion, is preferably returned as strip solution to stage (3) of the process of the present invention. Preferably the 40 conditions are selected such that the cuprous ion only is electrodeposited, since in this way the balance of the halide ion concentration is maintained. If excessive quantities of cupric ion are electrodeposited, additional quantities of halide ion will be transferred through the anion exchange membrane. Addition of further halide ion to the strip solution (spent electrolyte) may then be necessary to maintain the concentration of halide ion and prevent precipitation of cuprous chloride from the pregnant strip solution.

A corresponding split cell may be used for the recovery of cupric chloride leachant.

An alternative form of electrolytic cell which may be used to recover metallic copper consists of a conventional cell divided into anode and cathode compartments. The pregnant strip solution is fed to the cell and the cuprous ion is reduced to metallic copper at the cathode, whilst chlorine gas is evolved at the anode. 45 The evolved chlorine gas is preferably used to regenerate the ferrous ion (or cuprous ion) leachant remaining in the leach solution after the cuprous ion has been extracted in stage (1) of the process of the present invention. The regenerated ferric or cupric chloride leachant may be returned to process further ore.

In a completely different method of recovering copper from the pregnant strip solution, the strip stage (3) may be operated at elevated temperature, for example about 80°C, and the conditions selected such that the 50 pregnant strip solution is saturated (or supersaturated) with respect to cuprous ion. On cooling the pregnant strip solution to ambient temperature, cuprous chloride precipitates and may be removed by filtration. The filtrate is then returned to the process as barren strip solution. Metallic copper may be recovered from the precipitated cuprous chloride by conventional means, for example fused salt electrolysis or hydrogen reduction. Chlorine evolved during fused salt electrolysis may be used to regenerate ferrous chloride to ferric chloride (or cuprous chloride to cupric chloride) for return to leach further ore. Similarly hydrochloric acid evolved during hydrogen reduction may be used in admixture with air to regenerate ferrous ion to ferric.

It will be appreciated that the extraction and strip steps of the process of the present invention may each take place in two or more stages, and that it is preferred to recirculate solutions between the various steps of 60 the process as indicated above to give an integrated overall process. For a truly integrated process additional steps may be incorporated. For example it may be necessary to remove iron introduced into the system from the complex sulphide ore during leaching. Additional oxidation of ferrous iron may also be required to achieve stoichiometry. The removal of excess iron and the oxidation of any residual ferrous ion in the leachant may be achieved for example by air oxidation with the precipitation of hydrated ferric oxide.

65 The invention is illustrated by the following Examples in which all parts and percentages are by weight

unless otherwise stated.

Example 1

An aqueous solution containing 50.00 gpl of Cuprous ion (as cuprous chloride), 167.55 gpl of ferrous ion (as ferrous chloride) and 3.65 gpl of hydrochloric acid was agitated with an equal volume of a 0.5 Molar solution of the bis-isodecyl ester of pyridine 3,5-dicarboxylic acid in ESCAID 100, a low-aromatic content hydrocarbon solvent. The aqueous and organic layers were allowed to disengage and were separated. The resultant loaded organic solution contained 13.5 gpl cuprous ion and the depleted aqueous solution contained 36.1 gpl cuprous ion. The loaded organic solution was agitated with an equal volume of a strip solution containing 25.1 gpl cupric ion as cupric chloride. After disengagement and separation of the phases, the stripped organic phase was found to contain 5.2 gpl cuprous ion and the pregnant strip solution was found to contain 32.8 gpl of total copper ion. 5 10 10

Example 2

15 A continuous solvent extraction circuit was assembled consisting of laboratory scale mixer settler units arranged for 1 stage of extraction and 1 stage of stripping. 15 The aqueous feed solution had the following composition of metal ions:-

| | | | |
|----|---------|------------|----|
| 20 | cuprous | 47.5 gpl | 20 |
| | ferrous | 167.55 gpl | |

In addition, the solution contained 3.65 gpl hydrochloric acid, giving a total chloride ion concentration of 6.9 Moles per litre.

25 The organic extractant phase contained 0.5 Moles per litre of the bis isodecyl ester of pyridine 3,5-dicarboxylic acid dissolved in ESCAID 100, and the strip solution contained 23.5 gpl copper as cupric chloride and 18.3 gpl of hydrochloric acid. 25

The pumps and agitators in the circuit were started and the flow rates were adjusted to give an organic flow of 40 ml/min and aqueous flows of 20 ml/min (2:1 organic to aqueous ratio). After the circuit had been 30 running successfully for 5 hours, samples were removed from the raffinate from the extraction circuit and from the pregnant strip solution and were analysed for total copper content and, by atomic absorption spectroscopy, for the ratio of cuprous ion to cupric ion. The results were as follows: 30

| 35 | | Total copper gpl | cupric ion gpl | cuprous ion gpl | 35 |
|----|-------------------------|------------------|----------------|-----------------|----|
| | Aqueous feed | 47.5 | 0 | 47.5 | |
| 40 | Raffinate | 35.0 | 0 | 35.0 | 40 |
| | strip solution | 23.5 | 23.5 | 0 | |
| | Pregnant strip solution | 35.9 | 23.5 | 12.4 | |

45 CLAIMS 45

1. Process for recovering copper values from an aqueous solution containing cuprous and ferrous cations and halide or pseudo halide anions which comprises the steps of
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 - (2) separating from the aqueous phase the organic phase containing cuprous ion in the form of a halide- or pseudo halide-containing complex with the copper extractant; and
 - (3) contacting the organic phase containing the complex of cuprous ion with the extractant with an aqueous strip solution containing copper substantially in the form of the cupric ion and halide or pseudo-halide anion, whereby copper transfers from the organic phase into the aqueous strip solution, the relative concentrations of cupric ion and halide or pseudo-halide anion being such that the cuprous ion transferred into the aqueous strip solution is soluble therein.